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| 157 7590 08/15/2007 BAYER MATERIAL SCIENCE LLC 100 BAYER ROAD PITTSBURGH, PA 15205 | | | EXAMINER BOYKIN, TERRESSA M | |
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Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

Office Action Summary

Application No.

10/542,341

Applicant(s)

WEHRMANN ET AL.

Examiner

Terressa M. Boykin

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-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --
Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☒ Responsive to communication(s) filed on 14 July 2005.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 6-16 is/are pending in the application.
- 4a) Of the above claim(s) _____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) _____ is/are allowed.
- 6) ☒ Claim(s) 6-16 is/are rejected.
- 7) ☐ Claim(s) _____ is/are objected to.
- 8) ☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on _____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☒ All b) ☐ Some * c) ☐ None of:
1. ☒ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. _____.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).
- * See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- 1) ☒ Notice of References Cited (PTO-892)
- 2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)
- 3) ☒ Information Disclosure Statement(s) (PTO/SB/08)
Paper No(s)/Mail Date 7-14-5.
- 4) ☐ Interview Summary (PTO-413)
Paper No(s)/Mail Date. _____.
- 5) ☐ Notice of Informal Patent Application
- 6) ☐ Other: _____.

Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

Claims are rejected under 35 U.S.C. 102(a, b, or e) as being anticipated by

USP 4644053 discloses cyclic polycarbonate (or thiol analog) oligomer mixtures are prepared by the reaction of bishaloformates or their thio analogs or mixtures thereof with dihydroxy or dimercapto compounds, with alkali metal hydroxides and various amines. The oligomer mixtures may be converted to polycarbonates or their thiol analogs by a method which is particularly adaptable to integration with polycarbonate processing operations.

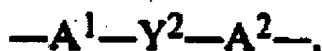
Polycarbonates are typically produced by the reaction of bisphenols with phosgene. This reaction is normally conducted interfacially; that is, in a mixed aqueous-organic system which results in recovery of the polycarbonate in the organic phase. Before the polycarbonate can be extruded, molded or otherwise worked, it must be freed of organic solvent and traces of water and by-products. It is then normally obtained as a solid which must be subjected to relatively cumbersome, high-temperature processing techniques.

The cyclic oligomer mixtures of this reference may contain organic carbonate, thiocarbonate and/or dithiocarbonate units. The various R values therein may be different but are usually the same, and may be aliphatic, alicyclic, aromatic or mixed; those which are aliphatic or alicyclic generally contain up to about 8 carbon atoms. Suitable R values include ethylene, propylene, trimethylene, tetramethylene, hexamethylene, dodecamethylene, 1,4-(2-butenylene), 1,10-(2-ethyldecylene), 1,3-cyclopentylene, 1,3-cyclohexylene, 1,4-cyclohexylene, m-phenylene, p-phenylene, 4,4'-biphenylene, 2,2-bis(4-phenylene)propane, benzene-1,4-dimethylene (which is a vinylog of the ethylene radical and has similar properties) and similar radicals such as those which correspond to the dihydroxy compounds disclosed by name or formula (generic or specific) in U.S. Also included are radicals containing non-hydrocarbon moieties. These

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may be substituents such as chloro, nitro, alkoxy and the like, and also linking radicals such as thio, sulfoxy, sulfone, ester, amide, ether and carbonyl. Most often, however, all R radicals are hydrocarbon radicals.

Preferably at least about 60% and more preferably at least about 80% of the total number of R values in the cyclic oligomer mixtures, and most desirably all of said R values, are aromatic. The aromatic R radicals preferably have the formula



wherein each of A¹ and A² is a single-ring divalent aromatic radical and Y² is a bridging radical in which one or two atoms separate A¹ from A². The free valence bonds in formula II are usually in the meta or para positions of A¹ and A² in relation to Y². Such R values may be considered as being derived from bisphenols of the formula HO--A¹--Y²--A²--OH. Frequent reference to bisphenols will be made hereinafter, but it should be understood that R values derived from suitable compounds other than bisphenols may be employed as appropriate.

(In formula II, the A¹ and A² values may be unsubstituted phenylene or substituted derivatives thereof, illustrative substituents (one or more) being alkyl, alkenyl (e.g., crosslinkable-graftable moieties such as vinyl and allyl), halo (especially chloro and/or bromo), nitro, alkoxy and the like. Unsubstituted phenylene radicals are preferred. Both A¹ and A² are preferably p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

The bridging radical, Y², is one in which one or two atoms, preferably one, separate A¹ from A². It is most often a hydrocarbon radical and particularly a saturated radical such as methylene, cyclohexylmethylene, 2-[2.2.1]-bicycloheptylmethylene, ethylene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene or adamantylidene, especially a gem-alkylene radical. Also included, however, are unsaturated radicals and radicals which are entirely or partially composed of atoms other than carbon and hydrogen. Examples of such radicals are 2,2-dichloroethylidene, carbonyl, thio and sulfone. For reasons of availability and particular suitability for the purposes of this invention, the preferred radical of formula II is the 2,2-bis(4-phenylene)propane radical, which is derived from bisphenol A and in which Y² is isopropylidene and A¹ and A² are each p-phenylene.

As noted, each Y¹ value is independently oxygen or sulfur. Most often, all Y¹ values are oxygen and the corresponding compositions are cyclic polycarbonate oligomer mixtures.

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When step II is necessary, the unwanted impurities may be removed in the necessary amounts by conventional operations such as combining the solution with a non -solvent for said impurities. Illustrative non -solvents include ketones such as acetone and methyl isobutyl ketone and esters such as methyl acetate and ethyl acetate. Acetone is a particularly preferred non -solvent.

The standards used for assignment of retention time and 254/280 value were separately prepared linear and cyclic polycarbonate oligomers of bisphenol A having degrees of polymerization of 2-5 and 3-6, respectively. The linear dimer was prepared by protecting one bisphenol A hydroxy group with a triethylsilyl moiety by reaction with triethylsilyl chloride, reacting two moles of the protected molecule with one mole of phosgene, and removing the protective moiety under acidic conditions. The linear trimer was prepared by a similar reaction in which bisphenol A bischloroformate was substituted for the phosgene. Reaction of one mole of the dimer and trimer with two moles of the monochloroformate of the protected bisphenol A, followed by removal of the protective moiety, yielded the linear oligomers with degrees of polymerization of 4 and 5, respectively. Each of these linear oligomers was then reacted with bisphenol A bischloroformate at high dilution to produce the cyclic oligomer having the next higher degree of polymerization.

The reaction conditions for Examples 1-18 are listed in Table I together with the approximate percentage (by weight) of cyclic polycarbonate oligomer present in the product before high polymer precipitation. The weight average molecular weights of the cyclic oligomer mixtures were approximately 1300, corresponding to an average degree of polymerization of about 5.1.

A solution of 1.4 mmol. of bisphenol A bischloroformate and 0.6 mmol. of 1,4-benzenedimethanol bischloroformate in 10 ml. of a tetrahydrofuran-methylene chloride solution comprising 10% by volume tetrahydrofuran was added over 30 minutes at 30.degree. C., with stirring, to a mixture of 10 ml. of methylene chloride, 2 ml. of 2.5M aqueous sodium hydroxide and 1 mmol. of triethylamine. After addition was complete, the mixture was washed three times with dilute aqueous hydrochloric acid and the organic layer was separated, dried by filtration through phase separation paper and evaporated under vacuum. The product was the desired mixed cyclic polycarbonate oligomer of bisphenol A and benzene-1,4-dimethanol.

Following the procedure of Example 20, products containing at least about 80% mixed cyclic polycarbonate oligomers were prepared from mixtures of bisphenol A bischloroformate and the dihydroxy compounds or dithiols listed in Table II. In each case, a total of 2 mmol. of reagent A was used. The proportion of the listed dihydroxy compound or dithiol was 10 mole percent unless otherwise indicated.

A solution of 3.10 mmol. of bisphenol A bischloroformate and 0.3 mmol. of bis(2-hydroxyphenyl)methane in 10 ml. of methylene chloride was added over 30 minutes at 25.degree., with stirring, to a mixture of 10 ml. of methylene chloride, 2 ml. of 2.5M aqueous sodium hydroxide and 0.5 mmol. of triethylamine. After addition was complete,

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the mixture was worked up as described in Examples 1-18. The product was the desired mixed cyclic polycarbonate oligomer of bisphenol A and bis(2-hydroxyphenyl)methane.

The crude bischloroformate product was added over one hour, with slow stirring, to a mixture of 200 ml. of 5M aqueous sodium hydroxide (1 mole) and 300 ml. of methylene chloride in a Morton flask. There was simultaneously added a solution of 5.05 grams (50 mmol.) of triethylamine in 20 ml. of methylene chloride. Stirring was continued for 15 minutes, after which the mixture was quenched by adding 3M aqueous hydrochloric acid to a pH of 3. The organic layer was washed twice with aqueous hydrochloric acid, dried over magnesium sulfate and vacuum stripped. There was obtained 48.94 grams of a white solid which was shown by high pressure liquid-liquid chromatography to comprise about 80% cyclic polycarbonate oligomers.

An amount thereof containing 800 mmol. of principal reagents, calculated as monomer bischloroformate, dissolved in one-half the total amount of methylene chloride used, was added over 37 minutes, with stirring, to a reaction vessel containing 450 ml. of 5M aqueous sodium hydroxide and the balance of the methylene chloride. The total amount of bischloroformate was 400 mmol. per liter of methylene chloride. Triethylamine, 200 mmol., was added incrementally at intervals of 25% during bischloroformate addition. The peak reaction temperature was 39.degree.. Upon workup as in Examples 1-18, there was obtained a product comprising 64% cyclic polycarbonate oligomers.

Amounts of a methylene chloride solution of said product and aqueous sodium hydroxide solution identical to those used in Example 35 were added over 34 minutes, with stirring, to the remainder of the methylene chloride. Triethylamine, 200 mmol., was added incrementally as in Example 34. The peak reaction temperature was 37.degree.. Upon workup, there was obtained a product comprising 69% cyclic polycarbonate oligomer.

Amounts of a methylene chloride solution of said product and aqueous sodium hydroxide solution identical to those used in Example 35 were added over 37 minutes, with stirring, to the remainder of the methylene chloride. Triethylamine, 200 mmol., was added incrementally as in Example 35. The peak reaction temperature was 40.degree.. Upon workup, there was obtained a product comprising 82% cyclic polycarbonate oligomer.

The cyclic oligomer mixtures of this invention are useful as intermediates for conversion to polycarbonates or their thiol analogs. Accordingly, the present invention includes a method for the preparation of a resinous composition which comprises contacting at least one of the previously defined cyclic oligomer mixtures with a polycarbonate formation catalyst at a temperature up to about 350.degree. C. The oligomer mixtures may frequently be employed in this method without separation of high polymer therefrom, but if desired, high polymer may be removed as previously described.

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Previously known methods for forming (e.g., molding) polycarbonates are often cumbersome because of the high viscosities of the polycarbonates. On the other hand, it has not been possible to integrate preparation methods involving the use of phosgene or various monomeric esters with forming operations because of the presence of volatile solvents such as methylene chloride or by-products such as phenol, during or after polymerization. the cyclic oligomer mixtures of this reference are liquid and have low viscosities. Moreover, they are substantially non-volatile at resin formation temperatures. Thus, it is possible to integrate resin formation therefrom with such forming operations. For example, the cyclic oligomer mixtures are simultaneously polymerized and molded upon application of heat to the mold. This method, and the molded articles produced thereby, constitute other embodiments of the reference.

Lewis acids useful as polycarbonate formation catalysts include dioctyltin oxide, triethanolaminititanium isopropoxide, tetra(2-ethylhexyl) titanate and polyvalent metal (especially titanium and aluminum) chelates such as bisisopropoxytitanium bisacetylacetonate and the bisisopropoxyaluminum salt of ethyl acetoacetate. Among the preferred catalysts are lithium stearate and bisisopropoxytitanium bisacetylacetonate.

Another essential component in the cyclic oligomer preparation method of this invention is a substantially non-polar organic liquid which forms a two-phase system with water. The identity of the liquid is not critical, provided it possesses the stated properties. Illustrative liquids are aromatic hydrocarbons such as toluene and xylene; substituted aromatic hydrocarbons such as chlorobenzene, o-dichlorobenzene and nitrobenzene; chlorinated aliphatic hydrocarbons such as chloroform and methylene chloride; and mixtures of the foregoing with ethers such as tetrahydrofuran.

The resin formation reaction is typically effected by merely contacting the cyclic oligomer mixture with the catalyst at temperatures up to 350.degree. C., preferably about 200.degree.-300.degree. C., until polymerization has proceeded to the extent desired. Although the use of a solvent is within the scope of the invention, it is generally not preferred. In general, the amount of catalyst used is about 0.001-1.0 mole percent based on oligomer mixture.

The conditions of the polymerization reaction may be varied to produce resinous compositions of various molecular weights and molecular weight distributions, i.e., Mw/Mn ratios), including resins having properties substantially the same as those of commercial bisphenol A polycarbonates. Molecular weight can be controlled by varying the amount of catalyst, with a decrease in said amount generally resulting in an increase in molecular weight, or by employing known chain transfer or endcapping agents, of which diphenyl carbonate is an example, typically in amounts up to about 2.5 mole percent based on oligomer mixture. It is also possible to produce resins having very low molecular weight distributions (i.e., Mw/Mn ratios), frequently approaching or lower than 2.0.

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The resin preparation method of this reference may be used to produce polymers of very high molecular weights, particularly when no endcapping agents are used. Values above 250,000 are readily attainable. Under certain conditions, resins with molecular weights in the 600,000-700,000 range, or even higher, may be prepared. While high molecular weight polycarbonates of this type are known, they have previously been of little use in molding operations because of their intractability under normal molding conditions. This property is irrelevant, however, when the cyclic oligomer mixtures of the present invention are used as polycarbonate precursors since said mixtures can be simultaneously polymerized and molded to produce articles which are very tough and resistant to severe temperature and solvent conditions.

Individual cyclic oligomers (for example, the dimer, trimer or tetramer) may be polymerized by similar procedures. Their use as polymer intermediates is generally not preferred, because their generally high melting points necessitate the use of solvents. However, it has been discovered that the rate of polymerization of the cyclic bisphenol A carbonate dimer of this invention is much higher than those of the corresponding trimer, tetramer or oligomer mixture. For example, under identical conditions of polymerization in 2,4-dichlorotoluene, the dimer was essentially completely polymerized in less than one hour, compared to 2-3 hours for the trimer and tetramer and a substantially more gradual reaction for the oligomer mixture.

More preferably, the preparation of the crude bischloroformate product takes place in the presence of aqueous alkali.

A crude cyclic bisphenol A polycarbonate oligomer mixture, having a weight average molecular weight of about 1340, prepared by a method similar to that of Examples 1-18 (excluding dissolution in tetrahydrofuran for chromatography purposes) but still containing the high polymer constituents, was heated under nitrogen at 300.degree. C. and a solution of catalyst in methylene chloride was added after about 3 minutes. In Examples 43-45, diphenyl carbonate was added to the oligomer mixture as an endcapping agent. Polymerization was allowed to continue for 10 minutes, after which the polycarbonate was removed, dissolved in methylene chloride, filtered and precipitated by the addition of methanol. The weight average molecular weight, intrinsic viscosity and glass transition temperature (T_g) were also determined. The relevant parameters and results are given in Table IV. Intrinsic viscosities (IV) were determined in chloroform at 25.degree. C.

Various catalysts were thoroughly mixed in a nitrogen atmosphere, with a cyclic bisphenol A polycarbonate oligomer mixture similar to that of Examples 41-46 but having a molecular weight of about 2600. In Examples 47 and 49, the catalysts were added as 0.1M solutions in toluene. The mixtures were heated under nitrogen at 250.degree. C. for three hours, after which the polycarbonates produced were dissolved in methylene chloride, precipitated by pouring into methanol and dried. The relevant parameters and results are given in Table V.

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Blends of catalyst and the cyclic bisphenol A polycarbonate oligomer mixture used in Examples 47-52 were prepared. In Examples 53-56, blending was achieved by dissolving oligomers and catalyst in dry methylene chloride, mixing and evaporating the solvent; in Examples 57-59, by thoroughly grinding together solid oligomer and catalyst. A 2-gram sample of each blend was charged to a circular mold having an inside diameter of 1 inch (2.54 cm.), which had been preheated to 250.degree. C. The mold was closed and heated at 250.degree. C. for 3 minutes without applied pressure and for an additional time under a force of 2 tons (1.8 metric tons). It was then opened and the polycarbonate disk was removed. It was homogeneous, tough and could not be broken by bending.

TABLE II; TABLE IV (i.e. molding); TABLE V

The resin preparation method of this invention may be used to produce polymers of very high molecular weights, particularly when no endcapping agents are used. Values above 250,000 are readily attainable. Under certain conditions, resins with molecular weights in the 600,000-700,000 range, or even higher, may be prepared. While high molecular weight polycarbonates of this type are known, they have previously been of little use in molding operations because of their intractability under normal molding conditions. This property is irrelevant, however, when the cyclic oligomer mixtures of the present invention are used as polycarbonate precursors since said mixtures can be simultaneously polymerized and molded to produce articles which are very tough and resistant to severe temperature and solvent conditions.

Thus, the reference discloses cyclic copolycarbonate a prepared from the same components as claimed by applicants and based on the similarities in resulting properties, and moieties used to prepare such, appears to conform structurally to the formula as claimed. *Since the disclosed are expressed differently, amounts, parameters they nevertheless appear to overlap those claimed and thus are not distinguishable over the prior art.* In view of the above, there appears to be no significant difference between the reference(s) and that which is claimed by applicant(s). Any differences not specifically mentioned appear to be conventional. Consequently, the claimed invention cannot be deemed as novel and accordingly is unpatentable.

Correspondence

Please note that the cited U.S. patents and patent application publications are available for download via the Office's PAIR. As an alternate source, all U.S. patents and patent application publications are available on the USPTO web site (www.uspto.gov), from the Office of Public Records and from commercial sources. Applicants may be referred to the Electronic Business Center (EBC) at <http://www.uspto.gov/ebc/index.html> or 1-866-217-9197.

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Any inquiry concerning this communication or earlier communications from the examiner should be directed to Examiner Terressa Boykin whose telephone number is 571 272-1069. The examiner can normally be reached on Monday through Friday from 6:30am to 3:00pm.

The fax phone number for the organization where this application or proceeding is assigned is 703-872-9306. The general information number for listings of personnel is (571-272-1700).

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Tmb


Examiner Terressa Boykin
Primary Examiner
Art Unit 1711